



# Magnesium complexes containing $\beta$ -ketiminate and $\beta$ -diketiminato ligands with dimethylamino substituents on the ligand core nitrogen atoms

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## ABSTRACT

Treatment of dibutylmagnesium with two equivalents of 4-(2,2-dimethylhydrazino)dimethylhydrazone-3-penten-2-one ( $L^1H$ ) in diethyl ether afforded  $Mg(L^1)_2$  (76%), which contains  $\eta^2-L^1$  ligands with tetrahedral coordination at the magnesium ion. Similar treatment of dibutylmagnesium with 4-(2,2-dimethylhydrazino)-3-penten-2-one ( $L^2H$ ) or 5-(2,2-dimethylhydrazino)-2,6-dimethyl-4-hepten-3-one ( $L^3H$ ) and 4-*tert*-butylpyridine (4-*t*Bupy) in diethyl ether afforded the octahedral complexes  $Mg(L^2)_2(4-tBupy)_2$  (85%) and  $Mg(L^3)_2(4-tBupy)_2$  (79%). Treatment of dibutylmagnesium with two equivalents of  $L^2H$  or  $L^3H$  in the absence of 4-*t*Bupy afforded  $[Mg(L^2)_2]_2$  and  $Mg(L^3)_2$ , however, these complexes were difficult to isolate due to the sticky nature of the crude products. A better synthetic approach entailed sublimation of  $Mg(L^2)_2(4-tBupy)_2$  or  $Mg(L^3)_2(4-tBupy)_2$  at 95–100 °C/0.05 Torr, which afforded  $[Mg(L^2)_2]_2$  (94%) and  $Mg(L^3)_2$  (80%) as colorless crystalline solids that were easily isolated. Treatment of  $[MgCp(CH_3)(OEt_2)]_2$  with two equivalents each of 4-*t*Bupy and  $L^1H$  afforded  $MgCp(L^1)(4-tBupy)$  (65%). Similar treatment of  $[MgCp(CH_3)(OEt_2)]_2$  with two equivalents of  $L^2H$  or  $L^3H$  afforded the dimeric complexes  $[MgCp(L^2)]_2$  (81%) and  $[MgCp(L^3)]_2$  (84%), respectively.  $[MgCp(L^2)]_2$  and  $[MgCp(L^3)]_2$  decompose upon attempted sublimation at 125–130 °C/0.05 Torr to afford  $Cp_2Mg$  (47–53%) and  $[Mg(L^2)_2]_2$  (67%) or  $Mg(L^3)_2$  (74%). The X-ray crystal structures of  $Mg(L^1)_2$ ,  $Mg(L^3)_2(4-tBupy)_2$ ,  $[Mg(L^2)_2]_2$ ,  $Mg(L^3)_2$ ,  $MgCp(L^1)(4-tBupy)$ ,  $[MgCp(L^2)]_2$ , and  $[MgCp(L^3)]_2$  are described. The thermal stability and volatility of the complexes were determined through preparative sublimation experiments. Many of the complexes sublime without decomposition at moderate temperatures and low pressures, and thus represent new potential precursors for thin film growth using chemical vapor deposition and related techniques.

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## 1. Introduction

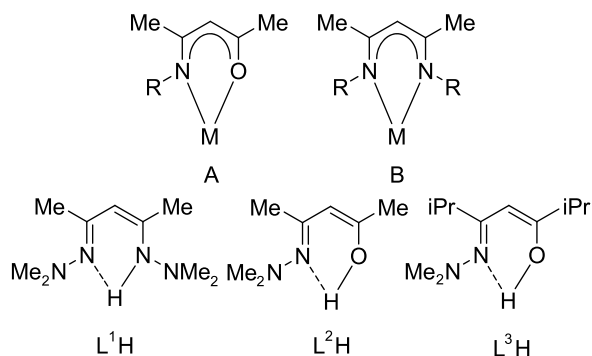
Magnesium complexes containing  $\beta$ -ketiminato (Chart 1, A) or  $\beta$ -diketiminato (Chart 1, B) ligands have been investigated for their interesting structural features [1], applications in polymerization catalysis [2], and as precursors for the growth of thin films by chemical vapor deposition (CVD) and related techniques [3,4]. Most of the crystallographically characterized complexes reported to date contain bulky aryl substituents on the ligand core nitrogen atoms [1,2]. Incorporation of aryl groups is less desirable for thin film precursor applications, since volatility tends to be reduced by the high molecular weights and increased lattice energies promoted by aryl group  $\pi$ -stacking interactions. We have recently reported the synthesis, structure, and properties of a series of magnesium  $\beta$ -diketiminato complexes containing *tert*-butyl or isopropyl substituents on the ligand core nitrogen atoms [1c]. In these complexes,  $\pi$ - or  $\eta^2$ -coordination modes were observed for the

$\beta$ -diketiminato ligands, and several of the complexes sublimed without decomposition at moderate temperatures under reduced pressure. This study suggested that magnesium complexes containing  $\beta$ -diketiminato ligands might serve as useful CVD precursors. To improve the precursor characteristics, we sought to modify the substituents in magnesium  $\beta$ -ketiminato and  $\beta$ -diketiminato complexes that might lead to increased volatility. It is well known that group 2  $\beta$ -diketonate complexes containing fluorinated alkyl groups are more volatile than related complexes with normal alkyl groups [5], presumably through reduction of lattice energies arising from intermolecular fluorine atom lone pair/lone pair repulsions. However, the presence of fluorine is a liability, since this element is easily incorporated into the thin films and can lead to changes in materials properties. In seeking to reduce lattice energies with non-fluorinated ligands, we envisioned that incorporation of dialkylamino groups within  $\beta$ -ketiminato and  $\beta$ -diketiminato ligands might mimic the lattice energy-lowering effects of fluoroalkyl groups without introducing deleterious elements such as fluorine.

Herein, we report the synthesis, structure, properties, and volatility of a series of magnesium complexes containing  $\beta$ -ketiminato and

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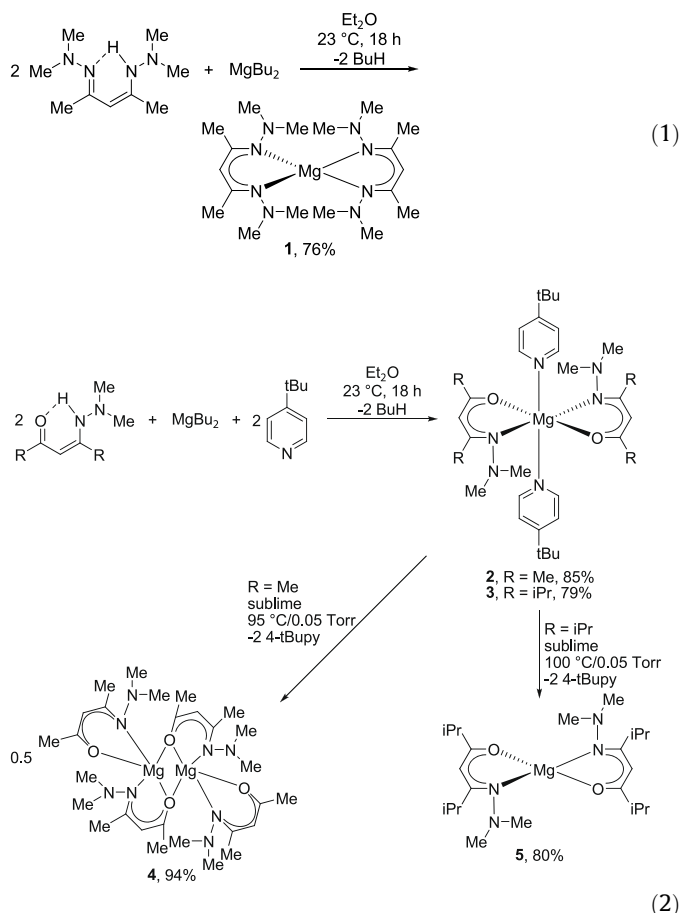
**Chart 1.**  $\beta$ -Diketiminato and  $\beta$ -ketiminato ligands and protonated precursors.

$\beta$ -diketiminato ligands derived from 4-(2,2-dimethylhydrazino)dimethylhydrazono-3-penten-2-one (Chart 1,  $L^1H$ ), 4-(2,2-dimethylhydrazino)-3-penten-2-one (Chart 1,  $L^2H$ ), and 5-(2,2-dimethylhydrazino)-2,6-dimethyl-4-hepten-3-one (Chart 1,  $L^3H$ ). These ligand precursors are easily prepared using literature procedures [6]. Using  $L^1H$ – $L^3H$ , various magnesium starting materials, and 4-*tert*-butylpyridine (4-*t*Bupy), monomeric and dimeric complexes of the formula  $MgL_2$ ,  $Mg(L^2)_2(4-tBupy)_2$ ,  $Mg(L^3)_2(4-tBupy)_2$ ,  $[MgL_2]_2$ ,  $MgL_2^3$ ,  $MgCp(L^1)(4-tBupy)$ ,  $[MgCp(L^2)]_2$ , and  $[MgCp(L^3)]_2$  were prepared and structurally characterized. Significantly,  $MgL_1^1$  sublimes at a much lower temperature than an analogous, previously reported magnesium  $\beta$ -diketiminato complex with isopropyl groups on the nitrogen atoms [1c], supporting the proposal that remote dimethylamino groups can increase volatility through reduction of lattice energy.

## 2. Results and discussion

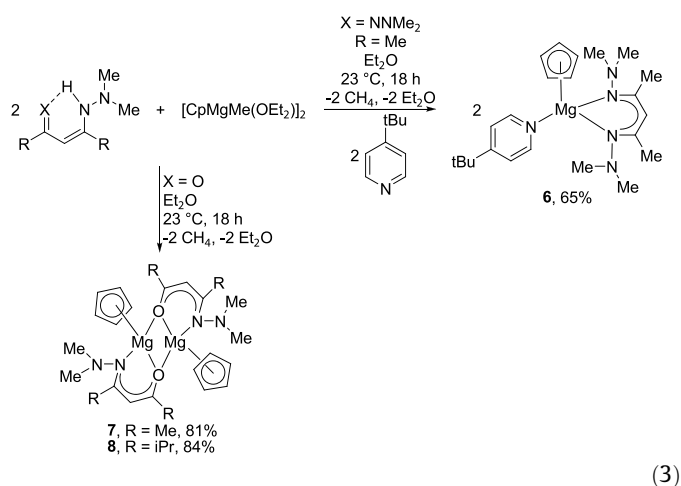
Treatment of dibutylmagnesium with two equivalents of  $L^1H$  in diethyl ether at ambient temperature led to elimination of butane and formation of  $Mg(L^1)_2$  (**1**, 76%) as a colorless solid (Eq. (1)). Repeating the synthesis of **1** in the presence of two equivalents of 4-*tert*-butylpyridine (4-*t*Bupy) did not afford a 4-*t*Bupy adduct, and only **1** was isolated. Analogous treatment of dibutylmagnesium with two equivalents of  $L^2H$  or  $L^3H$  in the presence of two equivalents of 4-*t*Bupy afforded  $Mg(L^2)_2(4-tBupy)_2$  (**2**, 85%) and  $Mg(L^3)_2(4-tBupy)_2$  (**3**, 79%) as colorless crystalline solids (Eq. (2)). Treatment of dibutylmagnesium with two equivalents of  $L^2H$  or  $L^3H$  in the absence of 4-*t*Bupy afforded the complexes  $[Mg(L^2)_2]_2$  (**4**) and  $Mg(L^3)_2$  (**5**) as sticky, colorless solids. Complexes **4** and **5** could not be crystallized from common solvents due to their high solubilities. Sublimation was an effective method for obtaining pure **4** and **5**, but the sticky nature of the crude solids led to variable, low yields due to losses during transfer to the sublimation tubes. A better approach entailed sublimation of **2** or **3** at 95–100 °C/0.05 Torr, which afforded **4** (94%) and **5** (80%) as colorless crystals through loss of the 4-*t*Bupy ligands (Eq. (2)). The structural assignments for **1**–**5** were based upon NMR spectroscopy, infrared spectroscopy, and C, H, N microanalyses, as well as X-ray crystal structure analyses (vide infra). The  $^1H$  NMR spectra of **1**–**5** in benzene- $d_6$  at 23 °C showed singlets for the  $\beta$ -CH fragment of  $L^1$ – $L^3$  between  $\delta$  4.32 and 5.01, while the  $\beta$ -carbon atom of  $L^1$ – $L^3$  in **1**–**5** resonated in the  $^{13}C\{^1H\}$  NMR spectrum between 86.97 and 96.17 ppm. Interestingly, all of the methyl groups in **5** are diastereotopic. In the  $^1H$  NMR spectrum of **5** at 23 °C in benzene- $d_6$ , a single resonance for the dimethylamino groups was observed at  $\delta$  2.34 and two types of isopropyl groups were observed. One of the isopropyl methyl resonances appeared as a normal doublet at  $\delta$  1.23, whereas the other isopropyl methyl resonance was a multiplet centered at  $\delta$  1.08. It is likely that the resonances for the

dimethylamino groups and one of the isopropyl methyl groups are accidentally degenerate and appear as a singlet and a normal doublet, respectively. The  $^{13}C\{^1H\}$  NMR spectrum at 23 °C in benzene- $d_6$ , however, clearly showed two resonances for the dimethylamino methyl groups at 48.68 and 47.53 ppm, two isopropyl methine resonances at 39.21 and 28.79 ppm, and four isopropyl methyl resonances at 22.15, 21.53, 21.36, and 21.18 ppm. Observation of diastereotopic methyl groups within the dimethylamino groups implies that inversion at the nitrogen atom is slow on the NMR timescale at 23 °C.

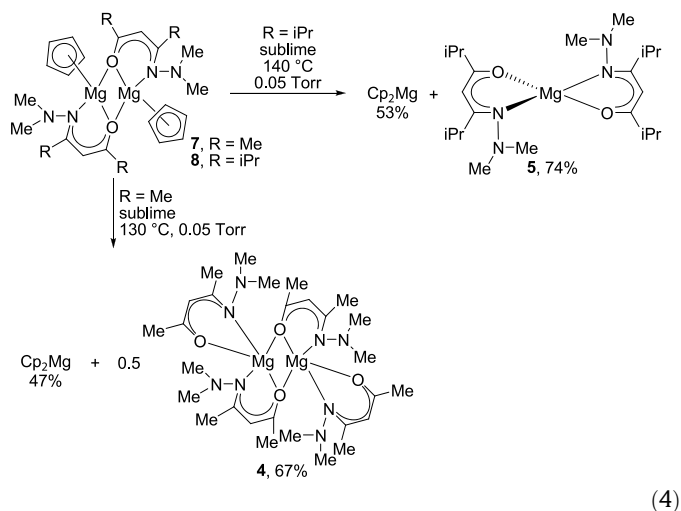


Treatment of  $L^1H$ ,  $L^2H$ , or  $L^3H$  (2 equivalents) with magnesocene ( $Cp_2Mg$ ) in diethyl ether at ambient temperature did not lead to any detectable reactions after 18 h. Accordingly, the stronger nucleophile  $[CpMgMe(Et_2O)]_2$  was employed instead of  $Cp_2Mg$ .  $[CpMgMe(Et_2O)]_2$  can be conveniently prepared by treatment of  $Cp_2Mg$  with dimethylmagnesium in diethyl ether according to a published procedure [7]. Treatment of  $[CpMgMe(Et_2O)]_2$  with  $L^1H$  (2 equivalents) in diethyl ether in the presence of two equivalents of 4-*t*Bupy afforded  $CpMg(L^1)(4-tBupy)$  (**6**, 65%) as a pale yellow crystalline solid (Eq. (3)). A similar reaction in the absence of 4-*t*Bupy led to a product that appeared to be  $CpMg(L^1)(Et_2O)$ , based upon its  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra. However, the diethyl ether ligand in  $CpMg(L^1)(Et_2O)$  was labile, and this complex decomposed slowly in the solid state to afford mixtures of  $Cp_2Mg$  and **1**. By contrast, **6** was stable toward loss of 4-*t*Bupy for greater than six months in the solid state at ambient temperature. Analogous treatment of  $[CpMgMe(Et_2O)]_2$  with two equivalents of  $L^2H$  or  $L^3H$  led to the dimeric complexes  $[CpMg(L^2)]_2$  (**7**, 81%) and  $[CpMg(L^3)]_2$  (**8**, 84%), which were isolated as colorless crystalline solids (Eq. (3)). The  $^1H$  NMR spectra of **6**–**8** in benzene- $d_6$  revealed singlets for the  $\beta$ -CH fragment of  $L^1$ – $L^3$  at  $\delta$  4.34, 4.68, and 5.02, respectively, while the

$^{13}\text{C}\{^1\text{H}\}$  NMR spectra showed resonances for the associated carbon atoms at 86.13, 100.53, and 90.94 ppm, respectively. These values are similar to those observed for **1–5**. Like **5**, **8** also exhibits diastereotopic isopropyl methyl groups, which appear in the  $^1\text{H}$  NMR spectrum in benzene- $d_6$  at 23 °C as a multiplet at  $\delta$  1.21 (12H) and doublets at  $\delta$  1.08 (6H) and 1.01 (6H). In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum in the same solvent, the isopropyl methine carbon atoms resonate at 38.97 and 29.38 ppm and the isopropyl methyl groups appear at 22.67, 21.21, 21.16, and 20.98 ppm. However, unlike **5**, the dimethylamino methyl groups of **8** appear as a single resonance in the  $^1\text{H}$  NMR spectrum at  $\delta$  2.55 and as a singlet in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at 48.71 ppm. It is likely that the coordination sphere in **8** is less crowded than that of **5**, which allows rapid inversion of the dimethylamino group nitrogen atom on the NMR time-scale in **8** and leads to methyl group site exchange. Upon cooling a toluene- $d_8$  solution of **8** to  $-60$  °C, the dimethylamino group resonance in the  $^1\text{H}$  NMR spectrum split into two singlets at  $\delta$  2.50 and 2.48, consistent with the proposed dimethylamino nitrogen atom inversion exchange mechanism. Interestingly, **3** does not exhibit diastereotopic methyl groups in its NMR spectra, since there is a plane of symmetry that passes through the  $L^3$  ligand cores and thus renders the methyl groups magnetically equivalent. The microanalysis data for **6–8** are consistent with the proposed formulations.



To assess their initial viability as film growth precursors, **1–8** were evaluated for their volatility and thermal stability. Sublimations were carried out at 0.05 Torr as described in Section 3. Complexes **1** and **6** sublimed at 90 °C and 110 °C with 91% and 75% recovery, respectively. The sublimation behavior of **2** and **3** was described above, and this approach represents the best syntheses of **4** and **5**. Once prepared, **4** and **5** resublimed between 90 and 95 °C at 0.05 Torr with 90% and 92% recovery, respectively. As outlined in Eq. (4), the unsymmetrical complexes **7** and **8** underwent ligand redistribution upon heating to 125–135 °C/0.05 Torr to afford sublimed  $\text{Cp}_2\text{Mg}$  (47–53%) and sublimed **4** (67%) or **5** (74%).



In order to establish the solid state geometries, the X-ray crystal structures of **1** and **3–8** were determined. Crystallographic data are summarized in Table 1. Selected bond distances and angles are given in Tables 2–7. Perspective views of **1** and **3–7** are shown in Figs. 1–6. The crystal structure of **2** could not be determined due to the low quality of the crystals. Its crystal structure is expected to be similar to that of **3**. The X-ray crystal structure of **8** was determined, but its molecular structure is very similar to that of **7** and is not discussed herein.

Complexes **1** and **5** are monomeric and possess distorted tetrahedral geometry about the magnesium ions. There are four independent molecules in **5** that exhibit identical structural features within experimental error. Only the molecule containing  $\text{Mg}(1)$

**Table 1**  
Crystal data and data collection parameters for **1** and **3–8**

|                                       | <b>1</b>                                 | <b>3</b>   | <b>4</b>  | <b>5</b>   | <b>6</b>                                 | <b>7</b>  | <b>8</b>  |
|---------------------------------------|--|--|---|--|--|---|---|
| Empirical formula                     | $\text{C}_{18}\text{H}_{38}\text{MgN}_8$ | $\text{C}_{40}\text{H}_{68}\text{MgN}_6\text{O}_2$ | $\text{C}_{28}\text{H}_{52}\text{Mg}_2\text{N}_8\text{O}_4$ | $\text{C}_{22}\text{H}_{42}\text{MgN}_4\text{O}_2$ | $\text{C}_{23}\text{H}_{37}\text{MgN}_5$ | $\text{C}_{24}\text{H}_{36}\text{Mg}_2\text{N}_4\text{O}_2$ | $\text{C}_{32}\text{H}_{52}\text{Mg}_2\text{N}_4\text{O}_2$ |
| Formula weight                        | 390.87                                   | 689.31   | 613.40  | 418.91   | 407.89                                   | 461.19  | 573.40  |
| Space group                           | $P2_1/c$                                 | $P2_1/n$   | $P2_1/c$  | $Cc$   | $Pna2_1$                                 | $P\bar{1}$  | $P2_1/n$  |
| <i>a</i> (Å)                          | 11.3337(3)                               | 12.8592(9)   | 18.0313(4)  | 19.7058(7)   | 12.8571(6)                               | 8.3312(3)   | 10.3557(12)   |
| <i>b</i> (Å)                          | 15.4438(5)                               | 18.1934(13)  | 18.3776(4)  | 19.7264(7)   | 13.4798(6)                               | 8.8303(3)   | 12.0802(13)   |
| <i>c</i> (Å)                          | 12.9708(4)                               | 18.6952(11)  | 10.5358(3)  | 27.0138(9)   | 13.9845(7)                               | 10.1814(6)  | 13.5668(15)   |
| $\alpha$ (deg)                        |  |  |   |  |  | 107.611(2)  |   |
| $\beta$ (deg)                         | 93.7820(10)                              | 104.055(4)   | 100.2990(10)  | 106.688(2)   |  | 98.779(2)   | 94.218(6)   |
| $\gamma$ (deg)                        |  |  |   |  |  | 111.654(2)  |   |
| <i>V</i> (Å <sup>3</sup> )            | 2265.40(12)                              | 4242.9(5)  | 3435.02(14)   | 10058.7(6)   | 2423.7(2)                                | 633.32(5)   | 1692.6(3)   |
| <i>Z</i>                              | 4  | 4  | 4   | 16   | 4  | 1   | 2   |
| Temperature (K)                       | 100(2)                                   | 100(2)   | 100(2)  | 100(2)   | 100(2)                                   | 100(2)  | 100(2)  |
| $\lambda$ (Å)                         | 0.71073                                  | 0.71073  | 0.71073   | 0.71073  | 0.71073                                  | 0.71073   | 0.71073   |
| Density calcd. (g/cm <sup>3</sup> )   | 1.146                                    | 1.079  | 1.186   | 1.106  | 1.118                                    | 1.209   | 1.125   |
| $\mu$ (mm <sup>-1</sup> )             | 0.098                                    | 0.080  | 0.113   | 0.093  | 0.091                                    | 0.122   | 0.103   |
| <i>R</i> ( <i>F</i> ) % <sup>a</sup>  | 3.92                                     | 4.68   | 4.36  | 6.42   | 3.79                                     | 3.35  | 4.77  |
| <i>Rw</i> ( <i>F</i> ) % <sup>b</sup> | 10.18                                    | 10.36  | 9.44  | 15.70  | 9.89                                     | 8.41  | 9.60  |

<sup>a</sup>  $R(F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$

<sup>b</sup>  $Rw(F)^2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}^{1/2}$  for  $l > 2\sigma(I)$ .

**Table 2**  
Selected bond lengths (Å) and angles (deg) for **1**

|              |           |
|--------------|-----------|
| Mg–N(1)      | 2.082(1)  |
| Mg–N(2)      | 2.076(1)  |
| Mg–N(5)      | 2.078(1)  |
| Mg–N(6)      | 2.070(1)  |
| N(1)–Mg–N(2) | 93.43(3)  |
| N(1)–Mg–N(5) | 118.08(3) |
| N(1)–Mg–N(6) | 125.27(4) |
| N(2)–Mg–N(5) | 110.84(4) |
| N(2)–Mg–N(6) | 117.16(4) |
| N(5)–Mg–N(6) | 93.23(3)  |

**Table 3**  
Selected bond lengths (Å) and angles (deg) for **3**

|              |           |
|--------------|-----------|
| Mg–N(1)      | 2.316(1)  |
| Mg–N(3)      | 2.297(1)  |
| Mg–N(5)      | 2.238(1)  |
| Mg–N(6)      | 2.247(1)  |
| Mg–O(1)      | 2.004(1)  |
| Mg–O(2)      | 2.009(1)  |
| N(1)–Mg–O(1) | 83.53(4)  |
| N(1)–Mg–O(2) | 96.00(4)  |
| N(1)–Mg–N(3) | 179.33(5) |
| N(1)–Mg–N(5) | 88.09(4)  |
| N(1)–Mg–N(6) | 89.79(4)  |
| O(1)–Mg–O(2) | 179.15(5) |
| O(1)–Mg–N(3) | 97.06(4)  |
| O(1)–Mg–N(5) | 89.80(4)  |
| O(1)–Mg–N(6) | 91.71(4)  |
| O(2)–Mg–N(3) | 83.41(4)  |
| O(2)–Mg–N(5) | 90.89(4)  |
| O(2)–Mg–N(6) | 87.58(4)  |
| N(3)–Mg–N(5) | 91.60(4)  |
| N(3)–Mg–N(6) | 90.51(4)  |
| N(5)–Mg–N(6) | 177.24(5) |

**Table 4**  
Selected bond lengths (Å) and angles (deg) for **4**

|                  |           |
|------------------|-----------|
| Mg(1)–N(1)       | 2.186(1)  |
| Mg(1)–N(3)       | 2.203(1)  |
| Mg(2)–N(5)       | 2.210(1)  |
| Mg(2)–N(7)       | 2.178(1)  |
| Mg(1)–O(1)       | 1.952(1)  |
| Mg(1)–O(2)       | 2.034(1)  |
| Mg(1)–O(3)       | 2.048(1)  |
| Mg(2)–O(2)       | 2.047(1)  |
| Mg(2)–O(3)       | 2.050(1)  |
| Mg(2)–O(4)       | 1.956(1)  |
| N(1)–Mg(1)–N(3)  | 128.83(5) |
| N(1)–Mg(1)–O(1)  | 86.32(5)  |
| N(1)–Mg(1)–O(2)  | 102.56(5) |
| N(1)–Mg(1)–O(3)  | 118.18(5) |
| N(3)–Mg(1)–O(1)  | 93.11(5)  |
| N(3)–Mg(1)–O(2)  | 82.93(5)  |
| N(3)–Mg(1)–O(3)  | 112.66(5) |
| O(1)–Mg(1)–O(2)  | 170.89(6) |
| O(1)–Mg(1)–O(3)  | 97.13(5)  |
| O(2)–Mg(1)–O(3)  | 77.01(5)  |
| N(7)–Mg(2)–N(5)  | 119.59(5) |
| N(7)–Mg(2)–O(2)  | 115.79(5) |
| N(7)–Mg(2)–O(3)  | 107.74(5) |
| N(7)–Mg(2)–O(4)  | 87.11(6)  |
| O(2)–Mg(2)–N(5)  | 124.40(5) |
| O(2)–Mg(2)–O(3)  | 76.67(5)  |
| O(2)–Mg(2)–O(4)  | 91.95(5)  |
| O(3)–Mg(2)–N(5)  | 82.50(5)  |
| O(3)–Mg(2)–O(4)  | 164.10(6) |
| O(4)–Mg(2)–N(5)  | 95.26(5)  |
| Mg(1)–O(2)–Mg(2) | 101.24(5) |
| Mg(1)–O(3)–Mg(2) | 100.70(5) |

**Table 5**  
Selected bond lengths (Å) and angles (deg) for **5**

|                 |          |
|-----------------|----------|
| Mg(1)–N(1)      | 2.088(3) |
| Mg(1)–N(3)      | 2.080(3) |
| Mg(1)–O(1)      | 1.916(3) |
| Mg(1)–O(2)      | 1.918(2) |
| N(1)–Mg(1)–O(1) | 91.9(1)  |
| N(1)–Mg(1)–O(2) | 114.5(1) |
| N(1)–Mg(1)–N(3) | 121.1(1) |
| O(1)–Mg(1)–O(2) | 122.1(1) |
| O(1)–Mg(1)–N(3) | 115.7(1) |
| O(2)–Mg(1)–N(3) | 94.0(1)  |

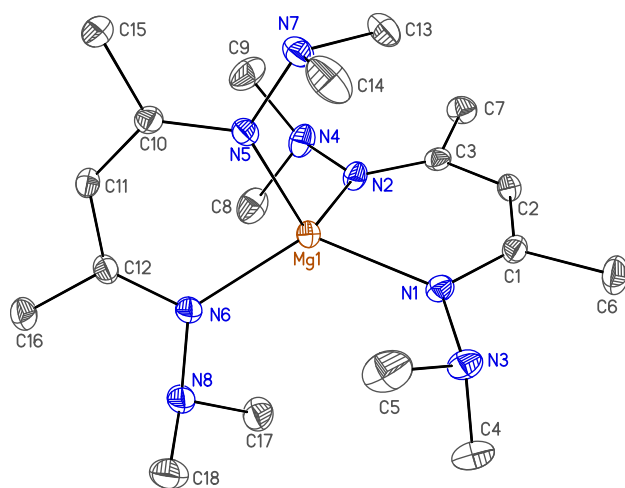
**Table 6**  
Selected bond lengths (Å) and angles (deg) for **6**

|              |            |
|--------------|------------|
| Mg–N(1)      | 2.175(1)   |
| Mg–N(2)      | 2.083(3)   |
| Mg–N(4)      | 2.091(3)   |
| Mg–C(10)     | 2.419(4)   |
| Mg–C(11)     | 2.406(4)   |
| Mg–C(12)     | 2.492(4)   |
| Mg–C(13)     | 2.565(1)   |
| Mg–C(14)     | 2.524(4)   |
| N(1)–Mg–N(2) | 99.29(11)  |
| N(1)–Mg–N(4) | 100.36(12) |
| N(2)–Mg–N(4) | 90.81(4)   |

**Table 7**  
Selected bond lengths (Å) and angles (deg) for **7**

|               |           |
|---------------|-----------|
| Mg–N(1)       | 2.142(1)  |
| Mg–O(1)       | 2.008(1)  |
| Mg–O(1)'      | 2.007(1)  |
| Mg–C(8)       | 2.434(1)  |
| Mg–C(9)       | 2.430(1)  |
| Mg–C(10)      | 2.445(1)  |
| Mg–C(11)      | 2.439(1)  |
| Mg–C(12)      | 2.434(1)  |
| N(1)–Mg–O(1)  | 87.87(4)  |
| N(1)–Mg–O(1)' | 105.89(4) |
| O(1)–Mg–O(1)' | 81.28(4)  |
| Mg–O(1)–Mg'   | 98.72(4)  |

will be presented herein. The magnesium–nitrogen bond distances in **1** range between 2.070(1) and 2.082(1) Å, while the corresponding values for **5** are between 2.080(3) and 2.088(3) Å. The magnesium–oxygen distances in **5** are 1.916(3) and 1.918(3) Å. The

**Fig. 1.** Perspective view of **1** with thermal ellipsoids at the 50% probability level.

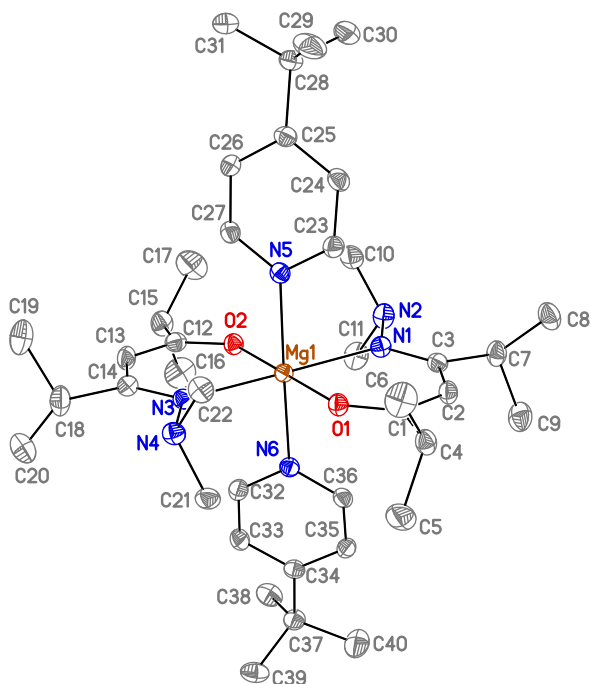


Fig. 2. Perspective view of **3** with thermal ellipsoids at the 50% probability level.

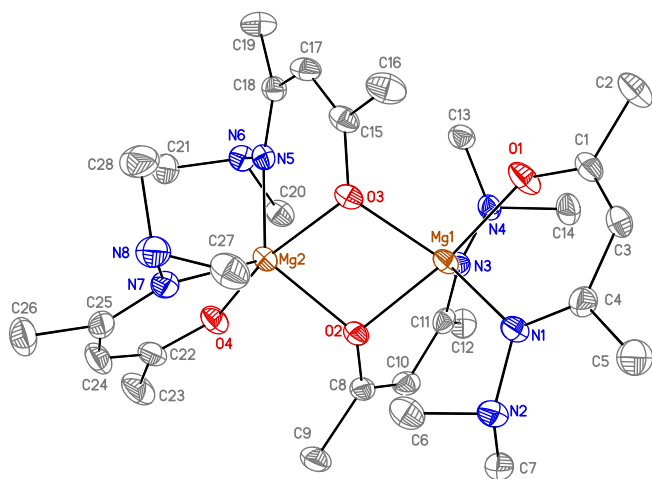


Fig. 3. Perspective view of **4** with thermal ellipsoids at the 50% probability level.

nitrogen–magnesium–nitrogen angles in **1** range between  $93.23(3)$  and  $125.27(4)^\circ$ , with an average of  $109.7^\circ$ . In **5**, the related coordination angles are between  $91.93(1)$  and  $122.07(1)^\circ$ , with an average of  $109.9^\circ$ . These average angles support the assignments as tetrahedral geometry. The nitrogen–carbon  $L^1$   $C_3N_2$  core distances in **1** are between  $1.326(1)$  and  $1.340(1)$  Å, and the carbon–carbon distances lie between  $1.404(1)$  and  $1.417(1)$  Å. These values are consistent with delocalized bonding among these atoms. In **5**, the carbon–nitrogen  $L^3$   $C_3NO$  core bond lengths are  $1.299(4)$  and  $1.320(4)$  Å, while the carbon–oxygen bond lengths are  $1.301(4)$  and  $1.311(4)$  Å. The carbon–carbon  $L^3$   $C_3NO$  core bond lengths are  $1.367(5)$ ,  $1.370(5)$ ,  $1.438(5)$ , and  $1.446(5)$  Å. The longer two bond lengths are associated with the carbon atoms bonded to the nitrogen atoms. These two types of bond distances differ significantly, and suggest a ligand structure containing an enolate-type donor connected by a carbon–carbon single bond to a carbon–nitrogen doubly-bonded hydrazone linkage.

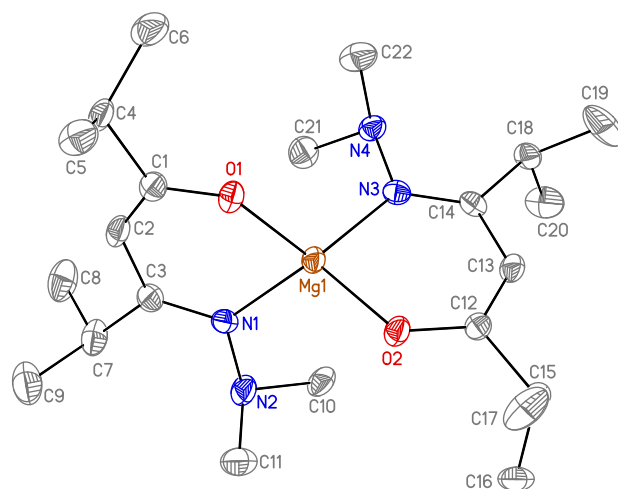


Fig. 4. Perspective view of **5** with thermal ellipsoids at the 50% probability level.

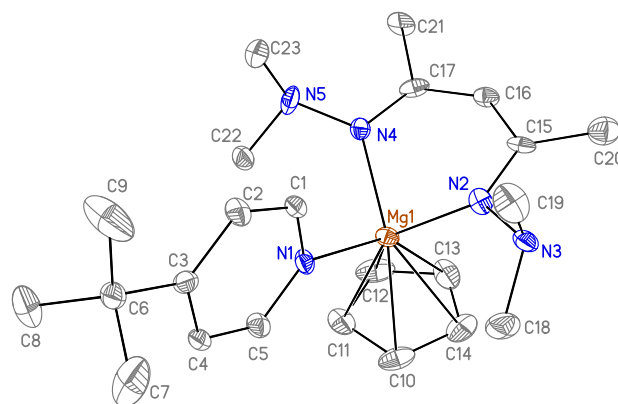


Fig. 5. Perspective view of **6** with thermal ellipsoids at the 50% probability level.

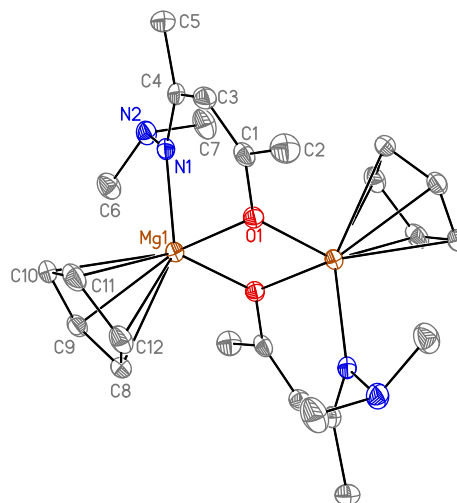


Fig. 6. Perspective view of **7** with thermal ellipsoids at the 50% probability level.

Complex **3** crystallizes as an octahedral monomer that contains two  $\eta^2$ - $L^3$  ligands within the equatorial plane and two *trans*  $\eta^1$ -4-tBupy ligands. The nitrogen and oxygen atoms are mutually *trans* within the equatorial plane. The magnesium–nitrogen and magnesium–oxygen distances associated with the  $L^3$  ligands are  $2.316(1)$

and 2.297(1) Å and 2.004(1) and 2.009(1) Å, respectively. The magnesium–nitrogen bond lengths associated with the 4-tBupy ligands are 2.238(1) and 2.247(1) Å, which are shorter than those of the formally anionic  $\beta$ -ketimate ligands. The magnesium–nitrogen and magnesium–oxygen bond distances in **3** are 0.09–0.24 Å longer than those observed in **5**, consistent with coordination numbers of six and four, respectively. The fact that the magnesium–nitrogen bond lengths associated with the  $\beta$ -ketimate ligand in **3** are longer than those of the neutral 4-tBupy ligands suggests that the  $\beta$ -ketimate nitrogen atoms serve as neutral donors, with the negative charge lying on the oxygen atoms. Within the  $L^3$  ligand  $C_3NO$  core, the carbon–nitrogen bond lengths are both 1.315(2) Å, while the carbon–oxygen bond lengths are both 1.292(2) Å. The carbon–carbon backbone bond lengths are 1.375(2), 1.376(2), 1.433(2), and 1.435(2) Å. These bond lengths are very similar to those observed in **5**, and suggest analogous  $\beta$ -ketimate ligand bonding arrangements in **3** and **5**.

Complex **4** crystallizes as a dimer, with one terminal  $\eta^2-L^2$  ligand and one  $\mu-\eta^1:\eta^2-L^2$  ligand per magnesium ion. The dimer is held together by a  $Mg_2O_2$  core. The coordination number at each magnesium ion is five. The magnesium–nitrogen distances range between 2.178(1) and 2.210(1) Å. The magnesium–nitrogen distances to the terminal  $\eta^2-L^2$  ligands are slightly shorter than those to the  $\mu-\eta^1:\eta^2-L^2$  ligands, although these differences are at the edge of experimental significance. The magnesium–oxygen distances to the terminal  $\eta^2-L^2$  ligands are 1.952(1) and 1.956(1) Å, while the values for the  $\mu-\eta^1:\eta^2-L^2$  ligands range between 2.034(1) and 2.050(1) Å. The magnesium–nitrogen and magnesium–oxygen bond distances are longer than those observed in four-coordinate **5** and shorter than those in six-coordinate **3**, consistent with the five-coordinate nature of **4**. The nitrogen–carbon bond lengths in the  $\beta$ -ketimate ligand core range between 1.308(2) and 1.315(2) Å, and are identical within experimental uncertainty for the two types of  $L^2$  ligands present. The oxygen–carbon bond lengths for the  $\eta^2-L^2$  ligand are 1.281(2) and 1.286(2) Å, and are 1.325(2) and 1.323(2) Å for the  $\mu-\eta^1:\eta^2-L^2$  ligand. These two types of bond lengths are different within experimental uncertainty, and probably reflect the extra magnesium–oxygen bonding associated with the bridging- $L^2$  oxygen atoms. Like **3** and **5**, the carbon–carbon distances in the  $L^2$  ligand cores range between 1.354(2) and 1.375(3) and 1.423(3) and 1.445(2) Å. The longer distances are associated with the nitrogen-bound carbon atoms, and there are no statistically significant differences between the  $\eta^2-L^2$  and  $\mu-\eta^1:\eta^2-L^2$  ligands.

Complex **6** crystallizes as a monomeric complex with approximately octahedral geometry about the magnesium ion, if the cyclopentadienyl ligand is considered to occupy three coordination sites. The coordination sphere contains an  $\eta^2$ -cyclopentadienyl ligand, an  $\eta^2-L^1$  ligand, and an  $\eta^1$ -4-tBupy ligand. The magnesium–nitrogen distances are 2.083(3) and 2.091(3) Å for the  $\eta^2-L^1$  ligand and 2.175(1) Å for the  $\eta^1$ -4-tBupy ligand. These values are shorter than the related bond distances in octahedral **3**, apparently because the coordination sphere in **6** is less crowded due to the compact cyclopentadienyl ligand. The magnesium–carbon distances for the cyclopentadienyl ligand are between 2.406(4) and 2.565(1) Å, and are distinctly asymmetric. The shortest magnesium–carbon distances are those syn- to the 4-tBupy ligand (C(10), C(11)), whereas the longer values are those further from the 4-tBupy ligand (C(12)–C(14)). Apparently, accommodation of the 4-tBupy ligand is achieved by distorting the cyclopentadienyl ligand coordination. The carbon–nitrogen distances within the  $L^1$  core are 1.294(4) and 1.359(4) Å, which are different within experimental uncertainty. In a similar fashion, the carbon–carbon bond lengths within the  $L^1$  core are asymmetric, with values of 1.380(6) and 1.447(6) Å. The asymmetric bond lengths within the  $L^1$  core of **6** are different than the delocalized bond lengths in the

$L^1$  ligands found in **1**, and are similar to the bond length alternations described above for the complexes containing  $L^2$  and  $L^3$  ligands. The nitrogen–magnesium–nitrogen angles range between 90.81(4) and 100.36(12)°, and average 96.82°. This average is slightly larger than the 90° value expected for ideal octahedral geometry, most likely due to the relatively small steric profile of the cyclopentadienyl ligand.

Complex **7** crystallizes as a dimeric molecule that is held together by a  $Mg_2O_2$  core. The overall structure of **7** is similar to that observed in **4**, except that  $\eta^5$ -cyclopentadienyl ligands have replaced the terminal  $\eta^2-L^2$  ligands. The overall geometry about each magnesium ion is distorted octahedral if the cyclopentadienyl ligand is considered to occupy three coordination sites. The  $L^2$  ligands adopt a  $\mu-\eta^1:\eta^2$ -coordination mode, similar to the bridging- $L^2$  ligand described above for **4**. The magnesium–nitrogen bond length is 2.142(1) Å, which is shorter than the related values in **4** but longer than those found in the  $L^1$  ligand of octahedral **6**. The magnesium–oxygen distances are 2.007(1) and 2.008(1) Å, which are shorter than the related values for **4**. The slightly shorter magnesium–nitrogen and magnesium–oxygen distances in **7** suggest that the coordination sphere in **7** is less crowded than that of **4**, even though **7** and **4** are formally six- and five-coordinate, respectively. The magnesium–carbon distances associated with the cyclopentadienyl ligand range between 2.430(1) and 2.445(1) Å, and are essentially identical within experimental uncertainty. The lack of asymmetry in the magnesium–carbon bond lengths of **7** suggests a sterically uncongested environment for the cyclopentadienyl ligand. The carbon–nitrogen bond length within the  $L^2$  ligand core is 1.306(2) Å, while the carbon–oxygen distance is 1.328(1) Å. The carbon–carbon backbone bond lengths are 1.357(2) and 1.457(2) Å, with the longer distance being associated with the nitrogen-bound carbon atom. This asymmetry is similar to the other complexes described above that contain  $L^2$  or  $L^3$  ligands. The nitrogen–magnesium–oxygen and oxygen–magnesium–oxygen angles are 87.87(4), 105.89(4), and 81.28(4)°, with an average value of 91.68°. This latter value is close to the expected 90° for octahedral geometry.

We have previously reported magnesium complexes containing N-isopropyl-4-(isopropylimino)-2-penten-2-amide ( $L^{iPr}$ ) ligands [**1c**], and the structural properties of these complexes can be compared with complexes described herein that contain  $L^1$ . In particular, the isopropyl and dimethylamino substituents on the nitrogen atoms of  $L^{iPr}$  and  $L^1$  are nearly identical in terms of size and molecular weight, so the structures and properties of analogous complexes should be very similar. Like **1**,  $Mg(L^{iPr})_2$  forms a monomeric complex with distorted tetrahedral geometry about the magnesium ion [**1c**]. The magnesium–nitrogen bond lengths in  $Mg(L^{iPr})_2$  (2.052(2)–2.065(2) Å) do not differ significantly from those in **1**, supporting a close structural analogy. Similarly, the structure and properties of  $CpMg(L^{iPr})(4-tBupy)$  are comparable to those of **6**, and both  $CpMg(L^1)(OEt_2)$  and  $CpMg(L^{iPr})(OEt_2)$  lose diethyl ether slowly to afford mixtures of  $Cp_2Mg$  and  $Mg(L^{iPr})_2$  or **1**. Thus, there is a strong structural and chemical resemblance between complexes containing  $L^1$  and  $L^{iPr}$  ligands.

A major difference between complexes containing  $L^{iPr}$  and  $L^1$  ligands relates to the sublimation temperatures of analogous complexes. For example,  $Mg(L^{iPr})_2$  sublimates at 160 °C/0.05 Torr [**1c**], while **1** sublimates at 90 °C/0.05 Torr at a similar rate. We propose that this astonishing difference in sublimation temperatures arises from the dimethylamino substituents in **1**, which reduce lattice energies through intermolecular repulsive interactions associated with the nitrogen-based lone pairs of electrons. This effect is similar to the volatility enhancements previously documented in group 2 complexes containing fluorinated alkyl groups [5]. However, **1** and related complexes do not contain fluorine, which eliminates a deleterious element from potential film growth precursor structures. It is possible that the volatility enhancement observed

in **1**, compared to  $\text{Mg}(\text{L}^{\text{IPr}})_2$ , is a general effect that can be used to impart increased volatility in film growth precursors for metals beyond group 2.

Several magnesium complexes containing  $\beta$ -ketiminate ligands have been structurally characterized [1a,2a,4]. Rees and coworkers reported a magnesium  $\beta$ -ketiminate complex containing a pendant 3-(dimethylamino)propyl substituent on each ligand core nitrogen atom [4]. The pendant dimethylamino groups coordinate to the magnesium center, creating a monomeric, octahedral complex with a structure similar to that of **3**. In the Rees complex, the magnesium–oxygen and magnesium–nitrogen bond lengths for the  $\beta$ -diketiminato ligand core are 2.018 and 2.162 Å, respectively, while the magnesium–nitrogen distance for the neutral dimethylamino donor is 2.393 Å. The magnesium–oxygen distances in **3** are very similar to those in Rees' complex, whereas the magnesium–nitrogen distances associated with the ligand core of **3** are about 0.15 Å longer. It is possible that the magnesium ion in **3** is more crowded sterically than that of Rees' complex, which leads to the longer magnesium–nitrogen distances in the former. Huang and coworkers [2a] reported the crystal structures of several monomeric four- and five-coordinate magnesium complexes that contain  $\beta$ -ketiminate ligands with a 2,6-diisopropylphenyl ( $\text{Ar}^*$ ) substituent on each nitrogen atom. Like **5**,  $\text{Mg}(\text{OC}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NAr}^*)_2$  has a distorted tetrahedral structure. The magnesium–oxygen and magnesium–nitrogen distances in  $\text{Mg}(\text{OC}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NAr}^*)_2$  are 1.8955(15) and 2.0589(15) Å, which are close to the values in **5** (Mg–O 1.916(3), 1.918(2) Å; Mg–N 2.080(3), 2.088(3) Å). There are no structurally characterized dimeric  $\beta$ -ketiminate complexes of magnesium that have been previously described, however, a trimeric complex has been reported [1a]. Like **4**, **7**, and **8**, the trimeric complex contains  $\mu$ - $\eta^1$ : $\eta^2$ - $\beta$ -ketiminate ligands in which the core oxygen atoms each bridge two magnesium ions. Similar  $\mu$ - $\eta^1$ : $\eta^2$ - $\beta$ -diketonate ligands were observed in the crystal structure of trimeric  $\text{Mg}_3(\text{acac})_6$  [8].

### 3. Experimental

#### 3.1. General considerations

All reactions were performed under argon using either glove box or Schlenk line techniques. Diethyl ether was freshly distilled from purple solutions of sodium benzophenone ketyl. Toluene was distilled from sodium. Hexane was distilled from  $\text{P}_2\text{O}_5$ .  $\text{Cp}_2\text{Mg}$  [9],  $\text{L}^1\text{H}$  [6],  $\text{L}^2\text{H}$  [6], and  $\text{L}^3\text{H}$  [6] were prepared according to the literature procedures.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained at 300 or 75 MHz in benzene- $d_6$  or toluene- $d_8$ , as indicated. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Micro-lab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected. X-ray crystal structure searches were conducted using version 5.29 (November 2007) of the Cambridge Crystallographic Database.

#### 3.2. Preparation of $\text{Mg}(\text{L}^1)_2$ (**1**)

A 100-mL Schlenk flask, equipped with a magnetic stir bar and a rubber septum, was charged with  $\text{L}^1\text{H}$  (0.862 g, 4.68 mmol) and diethyl ether (60 mL). To this stirred solution at  $-78^\circ\text{C}$  was added dibutylmagnesium (1 M in heptane, 2.34 mL, 2.34 mmol). The resultant light yellow solution was stirred at ambient temperature for 18 h. The volatile components were removed under reduced pressure to afford **1** (0.695 g, 76%) as a colorless crystalline solid: m.p. 128–130  $^\circ\text{C}$ ; IR (Nujol,  $\text{cm}^{-1}$ ) 1523 (s), 1284 (w), 1221 (m), 1158 (w), 1081 (w), 1021 (s), 989 (w), 917 (m), 848 (m), 657

(w);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ,  $\delta$ ) 4.32 (s, 2H,  $\beta$ -CH), 2.64 (s, 24 H,  $\text{N}(\text{CH}_3)_2$ ), 2.24 (s, 12H, C- $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ , ppm) 167.79 (s,  $\alpha$ -C), 87.08 (s,  $\beta$ -C), 48.57 (s,  $\text{N}(\text{CH}_3)_2$ ), 22.51 (s, C- $\text{CH}_3$ ).

Anal. Calc. for  $\text{C}_{18}\text{H}_{38}\text{MgN}_8$ : C, 55.31; H, 9.80; N, 28.67. Found: C, 55.17; H, 9.55; N, 28.76%.

#### 3.3. Preparation of $\text{Mg}(\text{L}^2)_2(4\text{-tBupy})_2$ (**2**)

A 100-mL Schlenk flask, equipped with a magnetic stir bar and a rubber septum, was charged with  $\text{L}^2\text{H}$  (0.333 g, 2.34 mmol) and diethyl ether (60 mL). To this stirred solution at  $-78^\circ\text{C}$  was added dibutylmagnesium (1 M in heptane, 1.17 mL, 1.17 mmol), followed by 4-*tert*-butylpyridine (0.340 mL, 2.34 mmol). A light yellow solution resulted upon warming to ambient temperature. The solution was stirred for 18 h at ambient temperature. Then, the volatile components were removed under reduced pressure to afford **2** (0.580 g, 85%) as a colorless crystalline solid: m.p. 95–97  $^\circ\text{C}$ ; IR (Nujol,  $\text{cm}^{-1}$ ) 1610 (w), 1584 (s), 1506 (w), 1416 (m), 1260 (s), 1230 (m), 1016 (m), 842 (m), 827 (s), 738 (m);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ,  $\delta$ ) 8.59 (m, 4H, 4-tBupy ring CH), 6.82 (m, 4H, 4-tBupy ring CH), 4.88 (s, 2H,  $\beta$ -CH), 2.51 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 2.10 (s, 6H,  $\text{CH}_3$ ), 2.05 (s, 6H,  $\text{CH}_3$ ), 0.98 (s, 18H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ , ppm) 178.92 (s,  $\alpha$ -C of  $\text{L}^2$ ), 174.18 (s,  $\alpha$ -C of  $\text{L}^2$ ), 159.24 (s,  $\gamma$ -C of 4-tBupy), 150.32 (s,  $\alpha$ -C of 4-tBupy), 120.59 (s,  $\beta$ -C of 4-tBupy), 96.08 (s,  $\beta$ -C of  $\text{L}^2$ ), 46.55 (s,  $\text{N}(\text{CH}_3)_2$ ), 34.27 (s,  $\text{C}(\text{CH}_3)_3$ ), 30.29 (s,  $\text{C}(\text{CH}_3)_3$ ), 27.18 (s, C- $\text{CH}_3$  of  $\text{L}^2$ ), 21.24 (s, C- $\text{CH}_3$  of  $\text{L}^2$ ).

Anal. Calc. for  $\text{C}_{32}\text{H}_{52}\text{MgN}_6\text{O}_2$ : C, 66.60; H, 9.08; N, 14.56. Found: C, 65.28; H, 8.84; N, 14.21%.

#### 3.4. Preparation of $\text{Mg}(\text{L}^3)_2(4\text{-tBupy})_2$ (**3**)

In a fashion similar to the preparation of **2**, treatment of  $\text{L}^3\text{H}$  (0.464 g, 2.34 mmol) with dibutylmagnesium (1 M in heptane, 1.17 mL, 1.17 mmol) and 4-*tert*-butylpyridine (0.34 mL, 2.34 mmol) afforded a clear light yellow solution upon reaching ambient temperature. After stirring for 18 h at ambient temperature, the volatile components were removed under reduced pressure. The crude colorless solid was dissolved in hexane (20 mL). The solution was filtered through a 1-cm pad of Celite on a coarse glass frit, and the filtrate was placed in a  $-25^\circ\text{C}$  freezer for 48 h to allow crystallization to occur. Removal of the solvent by cannula, followed by drying for 0.25 h at 0.05 Torr, afforded **3** (0.637 g, 79%) as a colorless crystalline solid: m.p. 118–120  $^\circ\text{C}$ ; IR (Nujol,  $\text{cm}^{-1}$ ) 1611 (m), 1573 (s), 1505 (w), 1487 (m), 1416 (w), 1378 (s), 1322 (w), 1275 (w), 1206 (m), 1090 (w), 1049 (w), 1016 (w), 935 (w), 845 (m), 767 (m);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ ,  $\delta$ ) 8.59 (m, 4H, 4-tBupy CH), 6.84 (m, 4H, 4-tBupy CH), 5.03 (s, 2H,  $\beta$ -H), 4.11 (septet,  $J = 6.0$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.54 (septet,  $J = 6.0$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.40 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 1.25 (d,  $J = 6.0$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.11 (d,  $J = 6.0$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 0.98 (s, 18H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23^\circ\text{C}$ , ppm) 188.52 (s,  $\alpha$ -C of  $\text{L}^3$ ), 183.42 (s,  $\alpha$ -C of  $\text{L}^3$ ), 159.17 (s,  $\gamma$ -C of 4-tBupy), 150.33 (s,  $\alpha$ -C of 4-tBupy), 120.53 (s,  $\beta$ -C of 4-tBupy), 87.34 (s,  $\beta$ -C of  $\text{L}^3$ ), 47.86 (s,  $\text{N}(\text{CH}_3)_2$ ), 39.20 (s,  $\text{CH}(\text{CH}_3)_2$ ), 34.27 (s,  $\text{C}(\text{CH}_3)_3$ ), 30.31 (s,  $\text{C}(\text{CH}_3)_3$ ), 28.81 (s,  $\text{CH}(\text{CH}_3)_2$ ), 21.92 (s,  $\text{CH}(\text{CH}_3)_2$ ), 21.34 (s,  $\text{CH}(\text{CH}_3)_2$ ).

Anal. Calc. for  $\text{C}_{40}\text{H}_{68}\text{MgN}_6\text{O}_2$ : C, 69.70; H, 9.94; N, 12.19. Found: C, 68.96; H, 9.62; N, 11.92%.

#### 3.5. Preparation of $[\text{Mg}(\text{L}^2)_2]_2$ (**4**)

A 30-cm long, 2.5-cm diameter glass tube was employed for the sublimation experiment. One end of the tube was sealed, and the other end had a 24/40 male glass joint, to which a vacuum pump was attached through a 24/40 vacuum adapter. A sample of **2** (0.500 g, 0.867 mmol) was placed at the sealed end of a glass tube

and a vacuum of 0.05 Torr was established. The glass tube was then placed in a horizontal Buchi Kugelrohr oven, such that about 15 cm of the tube was inside the furnace. The oven was heated to 95 °C, at which point sublimation of a colorless solid onto the cold portion of the tube was observed. After 1 h, sublimation was judged complete. Colorless crystals of **4** (0.247 g, 94%) were isolated by carefully scraping them from the sublimation tube with a spatula: m.p. 121–123 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1612 (w), 1578 (s), 1512 (s), 1414 (m), 1221 (m), 1212 (m), 1023 (s), 986 (m), 779 (m), 749 (s), 645 (m);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 4.84 (s, 4H,  $\beta\text{-CH}$ ), 2.45 (s, 24H,  $\text{N}(\text{CH}_3)_2$ ), 2.05 (s, 12H,  $\text{C-CH}_3$ ), 2.01 (s, 12H,  $\text{C-CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 192.59 (s,  $\alpha\text{-C}$  of  $\text{L}^2$ ), 174.19 (s,  $\alpha\text{-C}$  of  $\text{L}^2$ ), 96.28 (s,  $\beta\text{-C}$  of  $\text{L}^2$ ), 46.88 (s,  $\text{N}(\text{CH}_3)_2$ ), 27.13 (s,  $\text{C-CH}_3$ ), 21.02 (s,  $\text{C-CH}_3$ ).

Anal. Calc. for  $\text{C}_{28}\text{H}_{52}\text{Mg}_2\text{N}_6\text{O}_4$ : C, 54.83; H, 8.55; N, 18.27. Found: C, 54.62; H, 8.47; N, 18.28%.

### 3.6. Preparation of $\text{Mg}(\text{L}^3)_2$ (**5**)

In a fashion similar to the preparation of **4**, sublimation of **3** (0.501 g, 0.725 mmol) at 100 °C/0.05 Torr afforded **5** as colorless crystals (0.240 g, 80%): m.p. 116–117 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1574 (s), 1555 (m), 1506 (s), 1322 (s), 1298 (m), 1221 (m), 1203 (s), 1163 (m), 1154 (m), 1089 (s), 1020 (m), 921 (s), 898 (w), 777 (s), 743 (m), 690 (m), 628 (m);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 5.01 (s, 2H,  $\beta\text{-CH}$ ), 4.05 (septet,  $J = 5.4$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.51 (septet,  $J = 5.4$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.34 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 1.24 (d,  $J = 5.4$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.08 (m, 12H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 188.97 (s,  $\alpha\text{-C}$  of  $\text{L}^3$ ), 183.51 (s,  $\alpha\text{-C}$  of  $\text{L}^3$ ), 87.46 (s,  $\beta\text{-C}$  of  $\text{L}^3$ ), 48.68 (s,  $\text{N}(\text{CH}_3)(\text{CH}_3)'$ ), 47.56 (s,  $\text{N}(\text{CH}_3)(\text{CH}_3)''$ ), 39.21 (s,  $\text{CH}(\text{CH}_3)_2$ ), 28.79 (s,  $\text{CH}(\text{CH}_3)_2$ ), 22.15 (s,  $\text{CH}(\text{CH}_3)(\text{CH}_3)'$ ), 21.53 (s,  $\text{CH}(\text{CH}_3)(\text{CH}_3)''$ ), 21.36 (s,  $\text{CH}(\text{CH}_3)(\text{CH}_3)'$ ), 21.18 (s,  $\text{CH}(\text{CH}_3)(\text{CH}_3)''$ ).

Anal. Calc. for  $\text{C}_{22}\text{H}_{42}\text{MgN}_4\text{O}_2$ : C, 63.08; H, 10.11; N, 13.37. Found: C, 61.95; H, 9.97; N, 13.24%.

### 3.7. Preparation of $\text{MgCp}(\text{L}^1)(4\text{-tBupy})$ (**6**)

A 100-mL Schlenk flask, equipped with a magnetic stir bar and a rubber septum, was charged with  $\text{Cp}_2\text{Mg}$  (0.294 g, 1.90 mmol),  $\text{MgMe}_2$  (0.104 g, 1.90 mmol), and diethyl ether (40 mL). The mixture was stirred at ambient temperature for 2 h, at which point  $\text{L}^1\text{H}$  (0.70 g, 3.80 mmol) was added. The mixture was stirred at ambient temperature for 2 h, and then 4-*tert*-butylpyridine (0.561 mL, 3.80 mmol) was added. The final reaction mixture was stirred for an additional 18 h at ambient temperature. The volatile components were then removed under reduced pressure and the resultant mixture was dissolved in toluene (30 mL). The solution was concentrated to ~20 mL under reduced pressure and the flask was placed in a –25 °C freezer for 48 h to allow crystallization to occur. Removal of the solvent by cannula, followed by drying for 0.25 h at 0.05 Torr, afforded **6** (1.00 g, 65%) as pale yellow crystals: m.p. 201–203 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1611 (m), 1273 (w), 1225 (s), 1072 (w), 1017 (s), 984 (w), 917 (m), 844 (m), 760 (m);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 8.58 (m, 2H, 4-*t*Bupy CH), 6.74 (s, 5H,  $\text{C}_5\text{H}_5$ ), 6.67 (m, 2H, 4-*t*Bupy CH), 4.34 (s, 1H,  $\beta\text{-CH}$ ), 2.42 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 2.30 (s, 6H,  $\text{C-CH}_3$ ), 0.85 (s, 9H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 168.23 (s,  $\alpha\text{-C}$  of  $\text{L}^1$ ), 162.93 (s,  $\gamma\text{-C}$  of 4-*t*Bupy), 149.81 (s,  $\alpha\text{-C}$  of 4-*t*Bupy), 121.18 (s,  $\beta\text{-C}$  of 4-*t*Bupy), 106.43 (s,  $\text{C}_5\text{H}_5$ ), 86.13 (s,  $\beta\text{-C}$  of  $\text{L}^1$ ), 47.15 (s,  $\text{N}(\text{CH}_3)_2$ ), 34.60 (s,  $\text{C}(\text{CH}_3)_3$ ), 29.92 (s,  $\text{C}(\text{CH}_3)_3$ ), 22.79 (s,  $\text{C-CH}_3$ ).

Anal. Calc. for  $\text{C}_{23}\text{H}_{37}\text{MgN}_5$ : C, 67.73; H, 9.14; N, 17.17. Found: C, 67.47; H, 9.07; N, 16.85%.

### 3.8. Preparation of $[\text{MgCp}(\text{L}^2)]_2$ (**7**)

In a fashion similar to the preparation of **6**, treatment of  $\text{Cp}_2\text{Mg}$  (0.294 g, 1.90 mmol) with  $\text{MgMe}_2$  (0.104 g, 1.90 mmol) and  $\text{L}^2\text{H}$  (0.540 g, 3.80 mmol) afforded **7** (0.710 g, 81%) as colorless crystals after crystallization from toluene: m.p. 239–241 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 1613 (m), 1579 (m), 1528 (s), 1513 (m), 1404 (s), 1213 (m), 1093 (w), 1024 (s), 990 (m), 779 (m), 750 (m), 646 (m);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 6.18 (s, 10H,  $\text{C}_5\text{H}_5$ ), 4.69 (s, 2H,  $\beta\text{-CH}$ ), 2.45 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 1.89 (s, 6H,  $\text{CH}_3$ ), 1.73 (s, 6H,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 171.44 (s,  $\alpha\text{-C}$  of  $\text{L}^2$ ), 168.78 (s,  $\alpha\text{-C}$  of  $\text{L}^2$ ), 104.79 (s,  $\text{C}_5\text{H}_5$ ), 100.64 (s,  $\beta\text{-C}$  of  $\text{L}^2$ ), 47.87 (s,  $\text{N}(\text{CH}_3)_2$ ), 26.58 (s,  $\text{C-CH}_3$ ), 20.50 (s,  $\text{C-CH}_3$ ).

Anal. Calc. for  $\text{C}_{24}\text{H}_{36}\text{Mg}_2\text{N}_4\text{O}_2$ : C, 62.50; H, 7.87; N, 12.15. Found: C, 62.31; H, 7.80; N, 12.10%.

### 3.9. Preparation of $[\text{MgCp}(\text{L}^3)]_2$ (**8**)

In a fashion similar to the preparation of **6**, treatment of  $\text{Cp}_2\text{Mg}$  (0.294 g, 1.90 mmol) with  $\text{MgMe}_2$  (0.104 g, 1.90 mmol) and  $\text{L}^3\text{H}$  (0.750 g, 3.80 mmol) afforded **8** (0.910 g, 84%) as colorless crystals after crystallization from toluene: m.p. 250–252 °C; IR (Nujol,  $\text{cm}^{-1}$ ) 3085 (m), 1616 (s), 1597 (s), 1532 (s), 1365 (s), 1321 (w), 1201 (s), 1100 (s), 1027 (m), 1011 (m), 935 (m), 917 (m), 847 (m), 803 (m), 758 (s);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C,  $\delta$ ) 6.20 (s, 10H,  $\text{C}_5\text{H}_5$ ), 5.02 (s, 2H,  $\beta\text{-CH}$ ), 4.00 (septet,  $J = 7.0$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.55 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 2.31 (septet,  $J = 7.0$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.20 (m, 12H,  $\text{CH}(\text{CH}_3)(\text{CH}_3)'$ ), 1.08 (d, 6H,  $J = 7.0$  Hz,  $\text{CH}(\text{CH}_3)(\text{CH}_3)''$ ), 1.01 (d, 6H,  $J = 7.0$  Hz,  $\text{CH}(\text{CH}_3)(\text{CH}_3)'$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 23 °C, ppm) 180.99 (s,  $\alpha\text{-C}$  of  $\text{L}^3$ ), 179.17 (s,  $\alpha\text{-C}$  of  $\text{L}^3$ ), 104.92 (s,  $\text{C}_5\text{H}_5$ ), 90.76 (s,  $\beta\text{-C}$  of  $\text{L}^3$ ), 48.71 (s,  $\text{N}(\text{CH}_3)_2$ ), 38.97 (s,  $\text{CH}(\text{CH}_3)_2$ ), 29.38 (s,  $\text{CH}(\text{CH}_3)_2$ ), 22.67 (s,  $\text{CH}(\text{CH}_3)(\text{CH}_3)'$ ), 21.21 (s,  $\text{CH}(\text{CH}_3)(\text{CH}_3)''$ ), 21.16 (s,  $\text{CH}(\text{CH}_3)(\text{CH}_3)'$ ), 20.98 (s,  $\text{CH}(\text{CH}_3)(\text{CH}_3)''$ ).

Anal. Calc. for  $\text{C}_{32}\text{H}_{52}\text{Mg}_2\text{N}_4\text{O}_2$ : C, 67.03; H, 9.14; N, 9.77. Found: C, 67.12; H, 9.26; N, 9.88%.

### 3.10. Sublimation of **7**

A 2.5 cm diameter, 30 cm long glass tube was employed for the sublimation experiment. One end of the tube was sealed and the other end was equipped with a 24/40 male glass joint. In an argon-filled glove box, **7** (0.601 g) was loaded into a 0.5 × 2.5 cm glass tube and this tube was placed at the sealed end of the glass sublimation tube. The sublimation tube was fitted with a 24/40 vacuum adapter, and then was inserted into a horizontal Buchi Kugelrohr oven such that about 15 cm of the tube was situated in the oven. A vacuum of 0.05 Torr was established, and the oven was heated to 125 °C. The more volatile  $\text{Cp}_2\text{Mg}$  (0.106 g, 53%) collected in the glass tube just outside of the heated zone, while **4** (0.295 g, 74%) collected on the glass tube near the end of the heated zone. There was enough separation between the two sublimed materials to allow quantitation, but the yields were low due to losses during isolation.  $\text{Cp}_2\text{Mg}$  and **4** were identified by comparison of their  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra with those of authentic materials.

### 3.11. Sublimation of **8**

In a fashion similar to **7**, sublimation of **8** (0.501 g) at 130 °C/0.05 Torr afforded  $\text{Cp}_2\text{Mg}$  (0.063 g, 47%) and **5** (0.245 g, 67%) as colorless crystalline solids.  $\text{Cp}_2\text{Mg}$  and **5** were identified by comparison of their  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra with those of authentic materials.



### 3.12. Sublimations of **1** and **4–6**

Using the apparatus described for **7**, **1** and **4–6** were sublimed at 0.05 Torr at the temperatures and with the recoveries described in the text.

### 3.13. Crystallographic Structural Determinations of **1** and **3–8**

Diffraction data were measured on a Bruker X8 APEX-II kappa geometry diffractometer with Mo radiation and a graphite monochromator. Frames were collected at 100(2) K as a series of sweeps with the detector at 40 mm and 0.3° between each frame and were recorded for 3–10 s. APEX-II [10] and SHELX [11] software were used in the collection and refinement of the models. Further data for the structure determinations are presented in Table 1 and in the CIF files referenced below.

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### Appendix A. Supplementary material

CCDC 691628, 691629, 691630, 691631, 691632, 691633 and 691634 contains the supplementary crystallographic data for **1**, **3**, **4**, **5**, **6**, **7** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.08.022](https://doi.org/10.1016/j.jorganchem.2008.08.022).

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